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February 19, 2010

To the Office of Naval Research

Please find the attached progress report NM-001-ONR for awarded contract number N00014-10-C-0065 project. It summarizes the work conducted during the first quarter (100 days) of the project.

The following is applicable for this progress report:

Project Title: Advanced Lubrication for Energy Efficiency, Durability and Lower Maintenance Costs of Advanced Naval Components and Systems

Contract Number: N00014-10-C-0065

For the period from November 12, 2009 to February 19, 2010

CFDA Number: 12.300

CFDA Description: Basic and Applied Scientific Research

Sincerely,

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# Report Documentation Page

*Form Approved*
*OMB No. 0704-0188*



| | | |
|---|---|---|
| 1. REPORT DATE<br>**2010** | 2. REPORT TYPE | 3. DATES COVERED<br>**00-00-2010 to 00-00-2010** |
| 4. TITLE AND SUBTITLE<br>**Advanced Lubrication for Energy Efficiency, Durability and Lower Maintenance Costs of Advanced Naval Components and Systems** | | 5a. CONTRACT NUMBER<br>5b. GRANT NUMBER<br>5c. PROGRAM ELEMENT NUMBER |
| 6. AUTHOR(S) | | 5d. PROJECT NUMBER<br>5e. TASK NUMBER<br>5f. WORK UNIT NUMBER |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br>**NanoMech, LLC,535 W. Research Center Blvd, Suite 135,Fayetteville,AR,72701** | | 8. PERFORMING ORGANIZATION REPORT NUMBER |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | | 10. SPONSOR/MONITOR'S ACRONYM(S)<br>11. SPONSOR/MONITOR'S REPORT NUMBER(S) |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT<br>**Approved for public release; distribution unlimited** | | |
| 13. SUPPLEMENTARY NOTES | | |
| 14. ABSTRACT | | |
| 15. SUBJECT TERMS | | |

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT<br>**unclassified** | b. ABSTRACT<br>**unclassified** | c. THIS PAGE<br>**unclassified** | **Same as Report (SAR)** | **26** | |

Progress Report (1st quarter)

# Advanced Lubrication for Energy Efficiency, Durability and Lower Maintenance Costs of Advanced Naval Components and Systems

N00014-10-C-0065

Prepared for

Office of Naval Research

For the period

November 12, 2009 to February 19, 2010

Submitted by

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**Abstract**

In boundary lubrication, spacing of mating surfaces in direct physical contact is in the scale of surface asperities. These conditions may benefit from the nanoscale dimension of the advanced nanoparticle lubricants in the following ways: (1) by supplying nano to sub-micron size lubricating agents which reduce friction and wear at the asperity contact zone, (2) by enabling strong metal adsorption and easy wetting, (3) by reacting with the surface to form durable lubricating “transient transfer” films, sustain high loads and also retain under high temperatures, and (4) by enabling all these at minimal cost and great environmental safety. These materials specifically designed on antiwear and extreme pressure chemistries can significantly lower the sulfur and phosphorus level in the lubricant additive, and therefore provide environmental benefits.

The project encompasses a detailed investigation of advanced nanolubricants that favorably impact robust boundary film formation to reduce wear and friction. These active nanolubricant additives are designed as surface-stabilized nanomaterials that are dispersed in a hydrocarbon media for maximum effectiveness. This effort shall be focused on developing active nanoparticle composites, optimize process design, physical and chemical characterization of nanomaterials, detailed tribological film characterization, and tribological testing to document friction and wear improvements.

## Contents

## Summary

In this project we are developing extreme-pressure additives based on surface modified nano molybdenum sulfide ($MoS_2$). These additives are based on “green” surface chemistries used in the food industry combined with modified nano molybdenum sulfide and will have application in the many heavy duty lubrication systems used by the Navy, imparting lower friction, higher reliability and longer life, leading to reduced energy usage and increased mission availability. They will also have potential for use throughout industry.

In the first quarter of the project, we designed the model lubricant systems, acquired the pilot plant equipment for scale-up, and designed the experimental matrix. We identified commercial partners and set up industry standard tests that will be used to demonstrate the performance of these novel nanolubricant additives. The project is on track.

## Introduction

Friction, wear, and insufficient lubrication are major reasons for failure of vital engineering components and systems in Navy equipment (parts used in off- and on-shore systems, bearings, camshafts, pumps, etc.) [Kovalev, 2004]. Also, in addition to equipment failure, these issues cause excess energy consumption at impacting surfaces due to excessive friction and accelerated wear, caused by abrasive debris as a result of wear leading to reduced energy efficiency. For example, total frictional losses in a typical diesel engine may alone account for more than 10% of the total fuel energy (depending on the engine size, driving condition, etc.) [Fenske, 2006]. The failures due to friction and wear range across scale boundaries from nanoscale tribology at asperities to micro and macro scale tribology such as fretting and scuffing [Bhushan, 1999].

During the relative motion of two surfaces with lubricants in applications such as transmissions, pumps, bearings, piston rings, gears, engines, etc. three different lubrication stages may occur (Figure 1), and boundary layer lubrication is the most severe condition in terms of temperature and pressure. In boundary lubrication regime at low speeds, high temperatures and/or high loads, the protective film of lubricating oil becomes very thin and ruptures, so mating surfaces are in direct physical contact. Mating parts are exposed to severe contact conditions of high load, low velocity, extreme pressure and high local “flash temperature.” The stochastic behavior of the physical contact between the mating parts results in two problems: (1) abruptly exposing bare metal mating surfaces, and (2) the abrasive particles, which are produced as a result of friction & wear, aggravate the problem, significantly affecting the life of critical components.

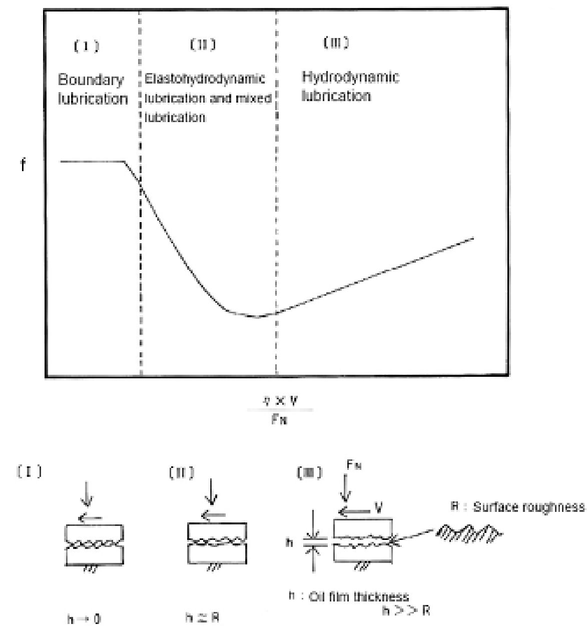


Figure 1. Stribeck curve and lubrication regions [Seiichro, 1984].

These conditions may benefit from novel advanced nanoparticle-based lubricants in the following ways: (1) by supplying nanoscale lubricating agents which reduce friction and wear at the intricate asperity-to- asperity contact zone, (2) by enabling strong tendency to adsorb uniformly on the surfaces and by offering easy wetting, (3) by reacting with the surface, so that durable lubricating “transient transfer” films are formed, which offer ability to sustain high loads and distribute the load locally as well as respond and sustain under high temperatures, and (4) by enabling all these at minimal cost and great environmental safety.

For these complex and dynamic conditions it becomes very important to understand what lines of defense can protect the machine and engine parts for an extended life. Various measures have been explored to address these challenges, particularly using extreme pressure (EP) additives, e.g. zinc dialkyl dithiophosphate (ZDDP), in formulated / synthetic oils. These EP additive molecules attach to open surfaces and are activated by the heat produced by friction at asperity-to-asperity contact due to sliding and rubbing, and chemically react with the surface to form a glassy phosphate film, preventing the surfaces from welding together. They provide good lubrication and anti-oxidation properties and as a result have been very commonly used for a couple of decades in various applications. However, their presence is typically not uniform in the contact zone due to the stochastic nature of the contact process. Thus, their formation is sporadic, resulting in uneven and rough surfaces. Further, this problem is exacerbated because it takes finite time and temperature for activation of these molecules, and thus the interim “dry start up period” results in major wear of the mating parts. Additionally, these current EP additives cause harmful emissions, and pose not only engineering challenges like poisoning the catalysts in some systems, but also environmental threats, according to new environmentally acceptable  emission standards.

Addressing critical lubrication for a range of engineering applications, including those of the Navy and other military and civilian applications would be extremely beneficial to economic wellbeing and environment [Koelsch, 1997]. Advanced lubricants in various forms such as solid (coating and particles as additives) and liquid (oils) and their combinations (the main focus of this project) can allow one to engineer systems that can improve productivity through energy savings and reliability of engineered systems [Bhushan, 1998]. For this project, the application systems of interest are severe friction and wear conditions under boundary layer lubrication regime, for example in heavy machinery, like pin-joints and major gear boxes in on- and off-shore equipment operation, to increase energy efficiency, increase durability and mission effectiveness, and reduce maintenance costs. These are of significant interest to the Navy and our industry partners.

This project focuses on development of challenging but high-payoff applications for the active family of nanolubricant additives, which is called NanoGlide®. In previous work, NanoMech has explored the fundamental science of nanoparticle design and synthesis using a top-down nanomanufacturing process, including the mechanisms of synthesis, interaction of "simple organic and inorganic materials" for deagglomerated nanostructures, dispersion stability, and preliminary tribological behavior, and promising results have been observed that give a solid foundation for realistic and valuable application-specific product development. Now the challenge is to experiment further with this concept to apply the underlying science in investigating the feasibility of NanoGlide application for preferred and versatile materials that are of importance and use in the current lubricant technology.

The findings from NanoMech's preliminary studies are of significant importance in the development of active nanoparticle-based lubricants, with outstanding lubrication properties responding to extreme pressure (EP) and related transient high temperature conditions [Komvopoulos, 2005], and at the same time, environmentally acceptable (EA) at low cost required in applications where boundary layer lubrication is crucial. Hence, from here onward the proposed active family of nanostructured lubricant additives will be referred to as Extreme Pressure-Environmentally Acceptable (active EP-EA) nanostructured lubricant additives (NanoGlide®) and their systematic fundamental study will be accomplished through the following technical tasks.

## Project Objectives

The high-level objective of this project is to develop nanoparticle-based additives to improve friction and wear characteristics of naval components and systems with a focus to enhance durability, energy efficiency, and maintenance costs of them.

To undertake this interdisciplinary feasibility project of significant defense, industrial, as well as fundamental importance, NanoMech with its expertise in nanomanufacturing science and engineering, nano surface chemistry, materials science, and tribology, adopted the following set of technical tasks for development of NanoGlide in this project that are based on project research plan (see Appendix, Table A1):

1. Design of application-specific active nanolubricants (NanoGlide);
2. Process scale up and nanomanufacturing of NanoGlide;
3. Synthesis, de-agglomeration and optimization of NanoGlide;
4. Structural, chemical and physical analysis of NanoGlide;
5. Tribological testing of NanoGlide;
6. Commercialization of NanoGlide.

## Project Scope

Through this project, the interaction with the available formulations will be studied to distinguish the effects of these unique additives in providing reduced friction and wear, and thus higher component life, as well as environmental and energy consumption benefits. It is well known that no new innovation in lubricant additive technology can be proven practical in the real sense until it can be shown to synergistically work with the complete formulation package. Therefore, for designing advanced lubricants, understanding the role of each component in the formulation is critical.

The project will develop application specific active nanostructures of inorganic dry solid lubricant intercalated with active organic molecules for lubricating oil. These materials shall consist of layered pressure sensitive inorganic nanoparticles of molybdenum disulfide ($MoS_2$) that is functionally attached to suitable organic temperature sensitive molecules that are effective in boundary lubrication. The resulting extreme pressure, environmentally acceptable (EP-EA) additive will be designed for low in ash, sulfur, and phosphorus content.

The effort shall include development and optimization of a chemo-mechanical process to generate multi-component nanoparticle additive systems that are suitably stabilized and dispersed in oil. Physical and chemical characterization of these materials shall be done using a range of microscopic and surface analytic tools. The focus shall be on understanding the inorganic-organic interface chemical behavior resulting in surface passivation and dispersion in hydrocarbon media. Extensive laboratory-based tribological evaluation of nanomaterials will be performed to document friction and wear characteristics in boundary lubrication regime. Effects of contact pressure, temperature and other test variables will be studied. Following bench test results, the EP-EA additive will be evaluated using single cylinder engine test to document efficiency and durability. Extensive market survey and industrial/economic impacts of nanoparticle based additive technology will be conducted.

## Major Activities

The research activities as outlined in the project plan (1st quarter, Table A1) for the funding phase November 12, 2009 – February 19, 2010 are noted below. The major activities of the team during this reporting period are:

**Task 1.** ***Designing of application-specific active nanolubricant (NanoGlide)*** (*Timeline for Task 1: November 2009 – August 2010*);

**Task 2.** ***Process scale up and nanomanufacturing NanoGlide*** (*Timeline for Task 2: January – August 2010*);

**Task 3.** ***Synthesis, de-agglomeration and optimization of NanoGlide*** (*Timeline for Task 3: January – August 2010*).

Specific tasks with timeline for deliverables and milestones to be performed by NanoMech including tasks for the University of Arkansas as a subcontractor and their progress are described below.

***Task 1: Designing of application-specific active nanolubricant (NanoGlide)***

The previous discussion has provided guidance on several considerations necessary for the design of an effective and well-understood boundary lubricant system in the application zone and thus, what kind of additive active EP-EA nanoparticle design is necessary to achieve that. In this task the project team will carefully select materials and design the application-specific active nanolubricant. This active EP-EA lubricant will meet the following criteria critical to meet the above design conditions: (1) inorganic particles nanometers in size, (2) intercalated with organic molecular medium to form nanocomposites, (3) assure they are well suspended in base oil medium, (4) assure their solubility, and (5) provide a source to form active lubricating films at the interacting surfaces. Deliverable for this task will be the material selection and design of the active nanolubricant.

*Subtask 1.1: Design and synthesis of multi-component nanolubricants (NanoMech and University of Arkansas)*

The goal is to design nanolubricant additives where nanoparticles of inorganic core are integrated with second component organic chemistry nanolubricants for naval application and develop lubricant additives for military oils.

Results and discussions

Based on the NanoMech's current understanding and experience on compounds that positively impact friction and wear characteristics, materials were selected for the designing stage. Molybdenum disulfide will form the core of the nanoparticle and will incorporate other phosphorus-based compounds in a stable surface stabilized composition. Amphiphilic molecules will help in this case, because they promote the formation of thin film and may help to demonstrate very low wear and friction characteristics. The other critical performance characteristics of the additive taken into consideration during discussion and selection of the active materials include antioxidation characteristics, hydrolytic stability, low ash forming composition, and environmental sustainability.

Two formulations are in progress of development for lubrication applications (additives to gear oils and greases) and are based on the developed and characterized formulations in the laboratory scale (NanoMech and University of Arkansas). The inorganic core consists of molybdenum disulfide ($MoS_2$) and organic molecular chemistries for integration include dialkyl dithiophosphate groups (DDP) or environmentally benign canola oil/phospholipid molecules.

These formulations are prepared by hybrid chemo-mechanical milling process for molybdenum sulfide ($MoS_2$) integrated with second element component to realize multi-component nanoparticle additives: (1) dialkyldithiophosphate (DDP)-functionalized molybdenum sulfide nanoparticles, and (2) $MoS_2$ nanoparticles integrated with organic canola oil fatty acid chains and phospholipids (Figure 2).

The application-specific active nanolubricant include (1) both hard, durable, load carrying components like phosphate layer, generated from metaloorganic polymeric complexes (e.g. zinc dialkyldithiophosphate) which can react with mating parts at high temperatures and (2) a softer, easily mechanically shearable components, pressure sensitive deformable (exfoliable) $MoS_2$ nanoparticles and resulting transfer film, along with organic integrated canola oil fatty acid chains and phospholipids.

*Experimental Procedure*

$MoS_2$ (98% purity) with average particle size (APS) of 3~5 μm was purchased from commercial suppliers. A mechanical shearing process was successfully used to reduce the primary particle size in dry conditions. During dry processing, due to increase in surface area at the submicron level, agglomeration is a major disadvantage and a major challenge to the development team. To alleviate the situation, chemo-mechanical approach was used to shear down the primary particles and to prevent agglomeration.

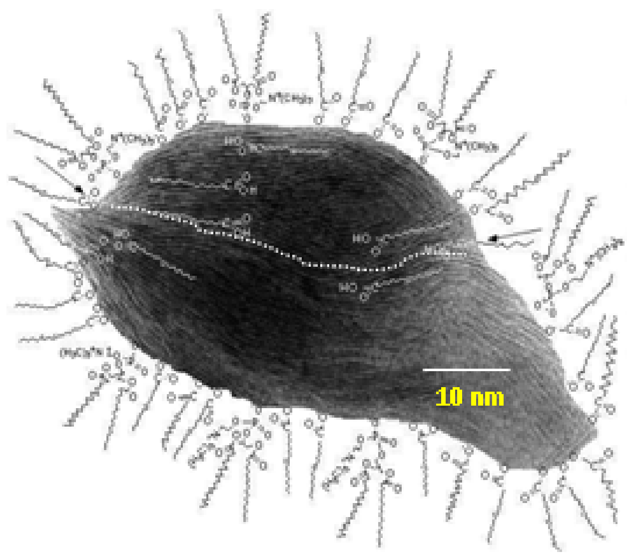


Figure 2. Proposed design of a typical active EP-EA $MoS_2$ nanoparticle with organic molecular capping and integration (figure shows TEM micrograph of the *real* particle with mechanically sheared and deformed atomic planes that is surrounded by Canola oil fatty acid molecules with interlinked bi-layers of phospholipid molecules shown in cartoon (not to scale))

The lab scale preparation method for nanoparticulate additive is based on high energy milling of $MoS_2$ involving fracture and extrusion mechanism [Malshe, 2008]. The milling process involves the shearing of the bulk particles to form smaller particles. The shape of these particles strongly depends on the milling process and the timelength of processing. The developed hybrid milling showed formation of uniform ellipsoidal particles with morphology resembling, “extruded” ends of the particle. The shape of particles may be in favor of their movement in the liquid media (similar to a fish shape). With longer milling time, particles have an increased extrusion like morphology, and in some cases are elongated significantly.

The hybrid milling process was a sequential combination of dry milling followed by a wet milling process (milling in liquid media). The combination of high energy milling to decrease the particle size in dry air ambient followed by milling in liquid ambient to prevent the particles from fusing, delivered samples containing ellipsoidal-shaped nanoparticles dispersed uniformly (Figure 3). The hybrid milling showed formation of uniform ellipsoidal particles with morphology resembling, “extruded” ends of the particle. The shape of particles may be in favor of their movement in the liquid media (similar to a fish). With longer milling time, particles have an increased extrusion like morphology, and in some cases are elongated significantly.

Detailed information on the milling mechanism for dry and wet steps, and hybrid process in full was described in patent applications [Malshe, patent applications, 2008]. In general, the 8-shaped rotation of vials, along with the path and interaction of balls in the vials causes the formation of spherical, elongated, open structure particles due to the squeezing and extrusion mechanisms. Initial particles underwent four mechanism scenarios during the milling process: (1) mechanical deformation of planar layers in lamellar structure on the $MoS_2$ on the tip of the particle, (2) breakage of the surface layers which were sticking out on the end of particle and extrude them to form squeezed endings, (3) conical shape of the particle tip with a long base interlayer and shorter layers closer to the surface caused by grinding and extrusion by milling media (vial walls and balls), and (4) formation of interlayered defects and layer dislocations at the particle endings.

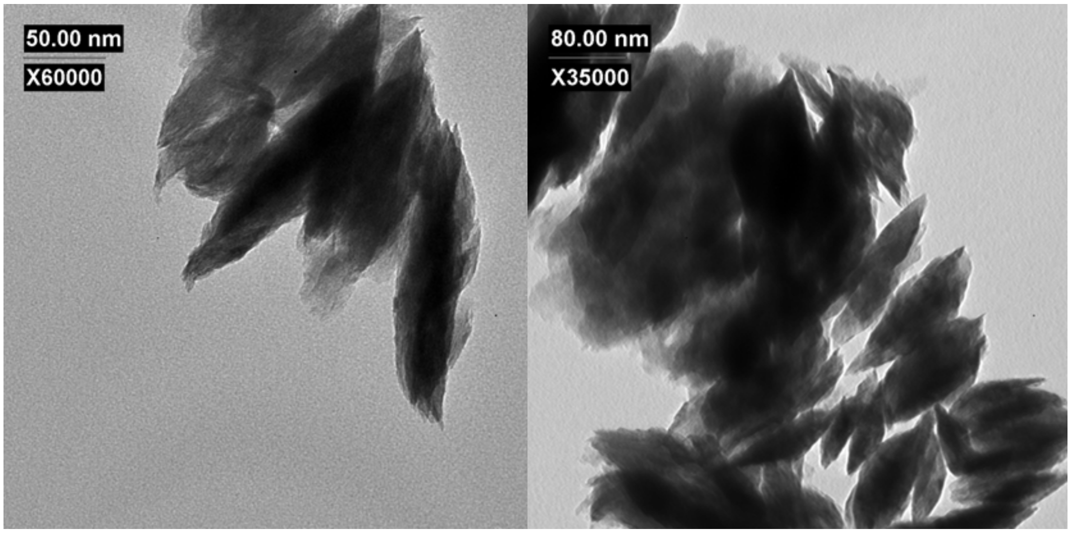


Figure 3. TEM graphs of $MoS_2$ sample prepared by hybrid chemo-mechanical milling process

These nanolubricants will address the diverse application needs of Navy, including lower coefficient of friction, smaller wear scar, high loading capability, good strength of tribofilm and equally important, little or no time to respond to “dry and harsh” conditions and deliver tribofilm as a result of plastic deformation, when trapped among asperities. Such application components of interest to Navy, for on- and off- shore purposes, are bearings, gear boxes, and engines.

**NOTE:** The detailed procedure of the chemomechanical process and the selection of the active chemical compounds are subjected to a US patent application and thus proprietary data and therefore not suitable for public release. The information is the core of the current funding period activity and is also based on our past experience in technology development in a related area of application. It is therefore advised to the reader to please contact the Principal Investigators or the Project Director for further information. Principal Investigators (Co-PIs) listed below may be contacted for further details regarding the project and portions covered by intellectual property clauses:

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Prof. Ajay P. Malshe [University of Arkansas, (479) 575 6561, apm2@uark.edu]

<u>Deliverables</u>

Accomplished deliverables:

1. Design of application specific active nanolubricants of interest to the Navy and potential Navy customers/collaborators;

2. Materials for synthesis of nanoparticles selected for application as additives in gear oils and greases.

Deliverables for 2nd quarter of the project:

1. Scale up of developed nanolubricant formulation synthesized by lab scale;
2. Synthesis and optimization of developed nanolubricant formulation by lab scale;
3. Structural, chemical and physical analysis of developed nanolubricant formulation.

***Task 2: Process scale up and nanomanufacturing of NanoGlide***

The process scale up task will maintain the objectives of process and material consistency whilst obtaining higher process yield in a pilot scale industrial process, low and affordable cost and the development of protocols for safe handling of the active EP-EA material.

One of the major benefits and uniqueness of this synthesis methodology is in using high energy milling, where the manufacturing platform, particularly for the high-energy ball milling process, is well established worldwide. The PIs will work with suitable equipment manufacturers and industry partners to put together a plan for scale up based upon findings of the fundamental research. Deliverable will be a description of the scale-up path and associated preliminary cost model.

Results and discussions

To facilitate large scale testing and also to support current project objectives, it is important to develop the process and pathway to scale-up beyond laboratory scale level. Based on the projected technical challenges involved in the scale-up activities and time involved in the same, the NanoMech's team considered this a priority and explored the process by pilot-testing at existing industrial-scale facilities.

The high-energy ball milling process (bench laboratory mill and pilot scale production mill) is planned to be used for particle size reduction and chemo-mechanical milling with the surrounding medium such as organic molecules.

The optimization of the scale up processing will be varied to achieve the outcome of similar morphological properties of samples synthesized in bench ball mill. Thus, milling time, milling media and material to milling media ratio will be variable parameters in pilot scale mill processing and the Design of Experiment (DoE) approach will be used to optimize these interdependent parameters to synthesize nanoparticles.

During the synthesis and optimization process one of the main objectives is to reduce milling time and obtain predictability in particle size, intercalation and capping consistency and uniformity of suspension (or de-agglomeration), which will further increase the efficiency and reduce the cost of making the process techno-economically possible when scaled up.

Important considerations in the scaled up operation are sealing of the mill, uniform distribution of the milling media, avoiding agglomeration of powder, controlling uniform temperature and periodic cleaning.

Deliverables

Accomplished Deliverables:

1. Production mill for scale up was selected and leased (2 months to build the mill, planned for delivery in February 2010);
2. Milling media was selected and purchased.

Deliverables for 2$^{nd}$ quarter of the project:

1. Synthesis of developed nanolubricant formulations by production mill scale;
2. Optimization of synthesized nanolubricant formulation for scale up;
3. De-agglomeration studies of synthesized nanolubricant formulation.

***Task 3: Synthesis, de-agglomeration and optimization of NanoGlide***

The unique, patent-pending process discovered by NanoMech will be used to synthesize the nanoparticles. In the proposed research, we will initially use lab-scale and then move up to large scale processing equipment at NanoMech to perform the synthesis, adjusting each of the critical variables in a Design of Experiment (DOE) approach to optimize the interdependent parameters. Deliverable from this task will be samples of the synthesized nanolubricant additive.

Results and discussions

The following update is mainly focused on the feasibility experiments and results based on the hybrid milling for synthesizing $MoS_2$ nanoparticles involving mechanical shearing process. The outcomes of this exploration are narrowed particle size distribution and shortened process time that contributed to the technical objective of extended shelf life of suspension stability, and commercial goal of increasing yield per batch with significantly reduction of the processing time.

The advantages of this hybrid process are that it not only reduces the particle size, but also retains the crystalline character of the $MoS_2$ particles. The process largely prevents crystal structure breakdown (amorphization) and lattice defects that are prone to occur in high-energy mechanical shearing process if run for significantly extended time without strictly controlling the gas environment.

For process optimization, the $MoS_2$ powder is planned to be chemo-mechanically milled for various time conditions, variable ball-to-powder ratios, and under various ambient conditions, starting with air, Canola oil, ZDDP, phospholipid and the subsequent combination of milling in air followed by milling in organic agents. The oil medium in the selected combination will be chosen to allow (a) homogeneous dispersion of particles inside the milling vial, thus avoiding particle clogging (b) utilizing mechanical energy to forge interaction between $MoS_2$ and organic agents to provide capping and intgration of organic molecules in $MoS_2$ nanoparticles and (c) capping with organic molecules, reduced agglomeration and preparing a uniform dispersion with the base oil.

The particle size of each batch of milled sample will be analyzed by use of a Horiba particle size analyzer, and the particle morphology will be analyzed using SEM and/or TEM. Based on the particle size differences, sedimentation rates, and agglomeration, the results for process optimizations will be compared and presented in the next reporting phase (second quarter report).

<u>Deliverables</u> for 2$^{nd}$ and 3$^{rd}$ quarters of the project:

1. Deign of experiments for synthesis and optimization for attritor milling;
2. Development of NanoGlide production procedure;
3. Development of product control procedures;
4. Synthesis of nanolubricants for naval applications;
5. Optimization of scale up milling.

***<u>Task 4</u>: Structural, chemical and physical analysis of nanostructures and inorganic-organic interfaces***

Complementary analytical techniques will be applied with particular objectives to study properties of synthesized nanoparticles (size and shapes, surface area, nanostructure and mechanical deformation due to milling, interfaces among inorganic and organic molecular media, and (5) chemical analysis of the milled $MoS_2$ products.

<u>Results and Discussions</u>

Analytical techniques will be used after tribological testing (see task 5) to study: (1) wear surface morphology, (2) chemistry and elemental distribution on wear tracks, (3) properties of various transfer layers on mating parts and other reaction products, and (4) size, morphology and surface chemistry of the debris.

X-ray diffraction (Rigaku D/Max) with Cu-Kα radiation will be used for the phase change analysis and size estimation after milling. Nanostructural analysis of the particles before and after milling will be carried out using a high resolution transmission electron microscopy (HRTEM; 2010 $LaB_6$ operating at 200kV and JEOL JEM-2100F FAST TEM). For TEM analysis of oil treated samples, organic solvents will be used to dissolve any physically adsorbed oil molecules that are not bonded strongly.

XPS (Kratos Axis ULTRA), FTIR and Raman spectroscopes will be performed to study the effect of the organic milling media on the particle surface chemistry modification. Philips XL 30 FEG scanning electron microscopy (SEM) and energy dispersive x-ray EDS analysis will be used for morphological and chemical analysis, for example of wear tracks after tribological testing to study phosphate complexes deposited. Surface area analysis, particle size analysis, and the stability of suspension will be tested using Quantachrome surface area analyzer (BET), Horiba particle size analyzer, and Sonas high resolution ultrasound spectrometer, respectively.

*Subtask 4.1:* Analysis and testing of structure-properties-application relationship *(University of Arkansas)*

This subtask will use a set of complementary analytical techniques to fundamentally understand behavior of the NanoGlide unique chemistries. The diagnosis of the above nanolubricants will involve chemical and structural analysis (XPS and TEM), tribological behavior (pin/ball-on-disc). The University of Arkansas will explore an active partnership with a leading Tribology group at the Naval Research Laboratory (NRL). The University of Arkansas will collaborate, through exchange of student, with Dr. Kathryn J. Wahl (NRL) in using a specially designed instrument at NRL for *in situ* friction and wear analysis. This tribology approach will allow learning behavior of nanolubricant at the nanoscale loading contact plastic behavior of nanoparticles using an optically transparent pin/ball. Raman signal tapped through the optically transparent pin/ball will carry the chemical signature of the event as it is occurring. This will give first hand insight in fundamental mechanism for behavior of the above novel chemistries.

Deliverables for 2$^{nd}$ and 3$^{rd}$ quarters of the project:

1. Characterization of NanoGlide nanolubricants;
2. Fundamental understanding of nanolubricants through chemical, structural, and tribological analysis;
3. Travel to UIUC for morphological and chemical analysis of tribofilms at CMM user facility.

***Task 5*: Tribological tests as a function of pressure (loading), speed, and temperature**

Fundamental and applied research will be conducted using bench-top tribological test setups (*pin-on-disc, four-ball, block on ring*) at varying loads, speeds to identify the behavior of these under different lubrication regimes (Stribeck curves), particularly focusing on the boundary lubrication condition with a broad loading and temperature range for clear understanding.

Results and Discussions

The lubrication performance of various oil blends formulated with application-specific active nanostructured $MoS_2$ (NanoGlide) at various additive concentrations (also see Task 6 for more details) will be studied through tribological testing. The test results will be used to generate friction and wear maps demonstrating the useful tribological performance under various pressures (loading), speed, and temperature conditions of active nanostructured $MoS_2$ mixed with base oils (non-formulated and formulated oils). The tribological testing and tribofilm analysis will clarify the behavior of each component in the oil blend, explaining the possible synergistic or antagonistic effect among them. This study will be the key observation in designing and developing the final nanoparticles based formulation for use in applications.

*Subtask 5.1:* Analysis and testing of structure-properties-application relationship *(University of Arkansas)*

The University of Arkansas will investigate the effects of nanolubricants addition into military gear oil using a test vehicle based on real gearbox housing and evaluate its performance.

They will explore use of various complementary analytical techniques to fundamentally understand the behavior of the chosen lubricant chemistries in support of the NanoMech task. In particular, the academic team will collaborate with the tribology group at Naval Research Laboratory to apply their specialized instrumentation for studying *in situ* friction and wear behavior.

Deliverables:

1. Design of experiments for tribological testing;
2. Tribological testing of NanoGlide samples pin/ball-on-disc, 4 ball test, block on ring];
3. Tribological testing of NanoGlide using a test vehicle based on real gearbox housing;
4. Travel to NRL for studying *in situ* friction and wear behavior;
5. Investigating the effects of nanolubricants addition into regular military gear oil and their tribological performance;
6. Understanding of nanolubricant behavior at the nanoscale loading contact;

***Task 6:*** **Commercialization of the NanoGlide Product Line**

NanoGlide is a family of extreme pressure additives with potential applications in a wide range of oils and greases. They will be supplied to formulators who will supply both military and commercial suppliers.

Results and Discussions

Potential customers supplying military lubricants were identified at the project kick-off meeting.

There are many potential commercial partners who also formulate for civilian applications – and we are working with a leading company in this field.

Standards for Lubricants include Military Specifications as well as standards developed by the ASTM (American Society for Testing Materials), SAE (Society of Automotive Engineers), API (American Petroleum Institute) and, internationally ILSAC (International Lubricant Standardization and Approval Committee).

There are many Mil Specs referring to both formulated lubricants and additives. One in particular, MIL-M-7866 (SAE AMS-M-7866) refers to Technical Molybdenum Disulfide at the 30 micron size scale (but not apparently at smaller scales). This may or may not be the basis for future standards.

We have prepared a commercialization checklist for the product to take it through the appropriate TRL and MRL levels as we refine and scale up the NanoGlide products.

NanoMech's approach to commercialize the NanoGlide family to the market is to first develop industry-credible performance data with one or more oil blenders that are seriously considering the use of NanoGlide. Oil and grease formulators are strong candidates to initially evaluate NanoMech's nanoparticle-based lubrication technology.

Once data is developed to validate the technology, NanoMech will market the NanoGlide family of additives to main oil formulators who work with the end users. NanoGlide® is a platform that can be used for production of nanoparticle-based formulations for different applications (additives to gear oils or engine oils).

Two strategies to validate the NanoGlide nanoparticle performance in oils and collect performance data include comparison of tribological performance for oil without nanoparticle addition and with nanoparticles and comparison of tribological performance for oils with higher viscosity without nanoparticles and oils with lower viscosity with nanoparticles.

Deliverables:

1. Design of experiments with parameter matrix for commercialization studies;
2. Calculations of production cost based on scale up progress;
3. Comparison and evaluation of NanoGlide additives/greases with market available oils/greases using analytical techniques and tribotesting.

## Conclusions

Nanolubricants will address the diverse application needs of Navy, including lower coefficient of friction, smaller wear scar, high loading capability, good strength of tribofilm and equally important, little or no time to respond to "dry and harsh" conditions and deliver tribofilm as a result of plastic deformation, when trapped among asperities. Such application components of interest to Navy, for on- and off- shore purposes, are bearings, gear boxes, and engines.

Based on the NanoMech's current understanding and experience on compounds that positively impact friction and wear characteristics, materials were selected for the designing stage. Molybdenum disulfide will form the core of the nanoparticle and will incorporate other phosphorus-based compounds in a stable surface stabilized composition. Amphiphilic molecules will help in this case, because it promotes the formation of thin film and may help to demonstrate very low wear and friction characteristics. The other critical performance characteristics of the additive taken into consideration during discussion and selection of the active materials are: antioxidation characteristics, hydrolytic stability, low ash forming composition, preferably environmentally sustainable, and such.

Two formulations are in progress of development for lubrication applications (additives to gear oils and greases) and are based on the developed and characterized formulations in the laboratory scale (NanoMech and University of Arkansas). The inorganic core consists of molybdenum disulfide ($MoS_2$) and organic molecular chemistries for integration include dialkyl dithiophosphate groups (DDP) or environmentally benign canola oil/phospholipid molecules.

The lab scale preparation method for nanoparticulate additive is based on high energy milling of $MoS_2$ involving fracture and extrusion mechanism. This milling process involves the shearing of the bulk particles to form smaller particles. The shape of these particles strongly depends on the milling process and the timelength of processing.

During the synthesis and optimization process one of the main objectives is to reduce milling time and obtain predictability in particle size, intercalation and capping consistency and uniformity of suspension (or de-agglomeration), which will further increase the efficiency and reduce the cost of making the process techno-economically possible when scaled up.

Two strategies to validate the NanoGlide nanoparticle performance in oils and collect performance data include comparison of tribological performance for oil without nanoparticle addition and with nanoparticles and comparison of tribological performance for oils with higher viscosity without nanoparticles and oils with lower viscosity with nanoparticles.

We have prepared a commercialization checklist for the product to take it through the appropriate TRL and MRL levels as we refine and scale up the NanoGlide products.

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## Cost and financial status

| Budget Period 1: | Budget | Actual |
|---|---|---|
| **NanoMech LLC** | $707,727 | $77,374.25 |
| **University of Arkansas** | $61,261 | $0 |
| **Total costs** | $768,988 | $77,374.25 |

### Subcontract negotiation status:

The project experienced an initial late start due to the negotiation of the actual contract between ONR and NanoMech LLC, and related subcontract agreement between NanoMech LLC and University of Arkansas. Currently the subcontractor agreement is completed and fully executed.

### Project kick off meeting:

According to project plan the kick of meeting was held for all involved personnel on December 11, 2009 to overview the project with a detailed project plan, including milestones, time schedules, specific responsibilities, and reporting requirements of each team member. The plan was discussed in detail at this meeting; team member input was recorded, considered, and incorporated into the plan. For the project progress, this plan will be used as a tracking tool to monitor progress against defined deliverables and milestones.

Lubrication applications (gears and greases) were identified and their lubrication benefits for navy applications were addressed. Military specifications and list of potential military consumers were discussed. These candidates were approached for evaluation of NanoGlide formulations.

### Publications and presentations:

We plan to attend the STLE (Society of Tribology and Lubrication Engineers) meeting in May and present a general paper “Advanced Nanolubricants for Loaded Components.” The main objectives at this meeting will be to connect with the potential customers / partners, determine which standards they need to work to (additive and / or final formulation) and pick the most receptive partners.

## Appendix: Proposed Research Plan

***<u>Task 1</u>: Designing of application-specific active nano lubricant and materials selection***

The previous discussion has provided guidance on several considerations necessary for the design of an effective and well-understood boundary lubricant system in the application zone and thus, what kind of additive active EP-EA nanoparticle design is necessary to achieve that. In this task the project team will carefully select materials and design the application-specific active nanolubricant. <u>This active EP-EA lubricant will meet the following criteria critical to meet the above design conditions: (1) inorganic particles nanometers in size, (2) intercalated with organic molecular medium to form nanocomposites, (3) assure they are well suspended in base oil medium, (4) assure their solubility, and (5) provide a source to form active lubricating films at the interacting surfaces</u>.

*<u>Subtask 1.1:</u> Design and synthesis of multi-component nanolubricants (NanoMech and University of Arkansas)*

The goal is to design nanolubricant additives where nanoparticles of inorganic core are integrated with second component organic chemistry nanolubricants for naval application and develop lubricant additives for military oils.

Deliverables:

1. Design of application specific active nanolubricants of interest to the Navy and potential Navy customers/collaborators is developed;
2. Materials for synthesis of nanoparticles are selected for application as additives in gear oils and greases.

***<u>Task 2</u>: Process scale up and nanomanufacturing considerations***

Last but not of the least importance is the critical task of nanomanufacturing process scale up. The process scale up task will keep the objectives of process and material consistency when obtaining higher process yields, low and affordable cost and protocols for safe handling of the active EP-EA material. One of the major benefits and uniqueness of this synthesis methodology is in use of a standard manufacturing platform, which is well established worldwide. The PIs will work with suitable equipment manufacturers and industry partners to put together a plan for scale up based upon findings of the fundamental research. Deliverable will be a description of the scale-up path and associated preliminary cost model.

Deliverables:

1. Selection of semi-industrial production mill for scale up;
2. Selection of milling media;
3. Synthesis of developed nanolubricant formulations by production mill scale;

4. Optimization of synthesized nanolubricant formulation for scale up;
5. De-agglomeration studies of synthesized nanolubricant formulation.

***<u>Task 3</u>*: *Synthesis, de-agglomeration and optimization of active EP-EA nanolubricant***

The unique, patent-pending process discovered by NanoMech will be used to synthesize the nanoparticles. In the proposed research, we will initially use lab-scale and then move up to large scale processing equipment at NanoMech to perform the synthesis, adjusting each of the critical variables in a Design of Experiment (DOE) approach to optimize the interdependent parameters.

Deliverables:

1. Deign of experiments for synthesis and optimization for attritor milling;
2. Development of NanoGlide production procedure;
3. Development of product control procedures;
4. Synthesis of nanolubricants for naval applications;
5. Optimization of scale up milling.

***<u>Task 4</u>*: *Structural, chemical and physical analysis of nanostructures and inorganic-organic interfaces***

Complementary analytical techniques will be applied with particular objectives to study properties of synthesized nanoparticles (size and shapes, surface area, nanostructure and mechanical deformation due to milling, interfaces among inorganic and organic molecular media, and (5) chemical analysis of the milled $MoS_2$ products.

Analytical techniques will be used after tribological testing (see task 5) to study: (1) wear surface morphology, (2) chemistry and elemental distribution on wear tracks, (3) properties of various transfer layers on mating parts and other reaction products, and (4) size, morphology and surface chemistry of the debris.

X-ray diffraction (Rigaku D/Max) with Cu-Kα radiation will be used for the phase change analysis and size estimation after milling. Nanostructural analysis of the particles before and after milling will be carried out using a high resolution transmission electron microscopy (HRTEM; 2010 $LaB_6$ operating at 200kV and JEOL JEM-2100F FAST TEM). For TEM analysis of oil treated samples, organic solvents will be used to dissolve any physically adsorbed oil molecules that are not bonded strongly.

XPS (Kratos Axis ULTRA), FTIR and Raman spectroscopes will be performed to study the effect of the organic milling media on the particle surface chemistry modification. Philips XL 30 FEG scanning electron microscopy (SEM) and energy dispersive x-ray EDS analysis will be used for morphological and chemical analysis, for example of wear tracks after tribological testing to study phosphate complexes deposited. Surface area analysis, particle size analysis, and the stability of suspension will be tested using Quantachrome surface area analyzer (BET), Horiba particle size analyzer, and Sonas high resolution ultrasound spectrometer, respectively.

*Subtask 4.1:* Analysis and testing of structure-properties-application relationship *(University of Arkansas)*

This subtask will use a set of complementary analytical techniques to fundamentally understand behavior of the NanoGlide unique chemistries. The diagnosis of the above nanolubricants will involve chemical and structural analysis (XPS and TEM), tribological behavior (pin/ball-on-disc). The University of Arkansas will explore an active partnership with a leading Tribology group at the Naval Research Laboratory (NRL). The University of Arkansas will collaborate, through exchange of student, with Dr. Kathryn J. Wahl (NRL) in using a specially designed instrument at NRL for *in situ* friction and wear analysis. This tribology approach will allow learning behavior of nanolubricant at the nanoscale loading contact plastic behavior of nanoparticles using an optically transparent pin/ball. Raman signal tapped through the optically transparent pin/ball will carry the chemical signature of the event as it is occurring. This will give first hand insight in fundamental mechanism for behavior of the above novel chemistries.

Deliverables:

1. Characterization of NanoGlide nanolubricants;
2. Fundamental understanding of nanolubricants through chemical, structural, and tribological analysis;
3. Travel to UIUC for morphological and chemical analysis of tribofilms at CMM user facility.

***Task 5*: Tribological tests as a function of pressure (loading), speed, and temperature**

The lubrication performance of various oil blends formulated with application-specific active nanostructured $MoS_2$ (NanoGlide) at various additive concentrations (also see task 6 for more details) will be studied through tribological testing. Applied work will be conducted using bench-top tribological test setups (*pin-on-disc, four-ball, block on ring*) at varying loads and speeds to identify the behavior of these under different lubrication regimes (Stribeck curves), particularly focusing on the boundary lubrication condition with a broad loading and temperature range for clear understanding. The test results will be used to generate friction and wear maps demonstrating the useful tribological performance under various pressures (loading), speed, and temperature conditions of active nanostructured $MoS_2$ mixed with base oils (non-formulated and formulated oils). The tribological testing and tribofilm analysis will clarify the behavior of each component in the oil blend, explaining the possible synergistic or antagonistic effect among them. This study will be the key observation in designing and developing the final nanoparticles based formulation for use in applications.

*Subtask 5.1:* Analysis and testing of structure-properties-application relationship *(MMRL, University of Arkansas)*

The University of Arkansas academic group will investigate the effects of nanolubricants addition into regular military gear oil using a test vehicle based on real gearbox housing and evaluate its performance.

They will explore use of various complementary analytical techniques to fundamentally understand the behavior of the chosen lubricant chemistries in support of the NanoMech task. In particular, the academic team will collaborate with the tribology group at Naval Research Laboratory to apply their specialized instrumentation for studying *in situ* friction and wear behavior.

Deliverables:

1. Design of experiments for tribological testing;
2. Tribological testing of NanoGlide samples pin/ball-on-disc, four ball test, block on ring];
3. Tribological testing of NanoGlide using a test vehicle based on real gearbox housing;
4. Travel to NRL for studying *in situ* friction and wear behavior;
5. Investigating the effects of nanolubricants addition into regular military gear oil and their tribological performance;
6. Understanding of nanolubricant behavior at the nanoscale loading contact;

***Task 6*:** **Commercialization of NanoGlide**

NanoMech's approach to commercialize NanoGlide to the market is to first develop industry-credible performance data with one or more lubricating oil compound/blenders that are seriously considering the use of NanoGlide. Oil and grease formulators produce large quantities of lubricants and several already have interest in NanoGlide. These formulators are strong candidates to initially evaluate NanoMech's nanoparticle-based lubrication technology.

Once data is developed to validate the technology, NanoMech will market the family of NanoGlide additives to main oil formulators who work with the end users. NanoGlide® is a platform that can be used for production of nanoparticle-based formulations for different applications (additives to gear oils or engine oils).

Two strategies to validate the NanoGlide nanoparticle performance in oils and collect performance data include comparison of tribological performance for oil without nanoparticle addition and with nanoparticles and comparison of tribological performance for oils with higher viscosity without nanoparticles and oils with lower viscosity with nanoparticles.

Deliverables:

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3. Comparison and evaluation of NanoGlide additives/greases with market available oils/greases using analytical techniques and tribotesting.

Table A1: Project Task Table

| | **Tasks** | **MONTH 1-2** | **MONTH 3-4** | **MONTH 5-6** | **MONTH 7-8** | **MONTH 9-10** | **MONTH 11-12** |
|---|---|---|---|---|---|---|---|
| 1. | ***Designing of application-specific active nanolubricant (NanoGlide)*** | | | | | | |
| 2. | ***Process scale up and nanomanufacturing NanoGlide*** | | | | | | |
| 3. | ***Synthesis, de-agglomeration and optimization of NanoGlide*** | | | | | | |
| 4. | ***Structural, chemical and physical analysis of NanoGlide*** | | | | | | |
| 5. | ***Tribological testing of NanoGlide*** | | | | | | |
| 6. | ***Commercialization of NanoGlide*** | | | | | | |